(2) Synthesis of bis(methylsulfonyl)diazomethane

Using bis(methylsulfonyl)methane (7.5 g, 0.04 mole) obtained in above (1), the reaction was carried out in the same manner as described in Example 1, (2), and the crude solid (4.5 g) was chromatographed on silica gel (Wakogel C-200) with n-hexane/ethyl acetate (8/1 → 4/1 → 3/1) as eluent to give 2.5 g of bis(methylsulfonyl)diazomethane as white crystals.

m.p.: 120°–124° C.

^{1}HNMR δ ppm ($CDCl_3$): 3.37 (6H, s, $CH_3 \times 2$).

IR (KBr-disk) ν cm^{-1}: 2145 (CN_2), 1335, 1320.

APPLICATION EXAMPLE 1

A resist material having the following composition was prepared:

Poly(p-tert-butoxystyrene-p-hydroxystyrene) [Polymer obtained in Reference Example 1, (2)]	6.0 g
Bis(cyclohexylsulfonyl)diazomethane [Photoacid generator obtained in Example 1, (2)]	0.3 g
Diethylene glycol dimethyl ether	13.7 g

Using the resist material, a pattern was formed as shown in FIG. 2. That is, the resist material was spin coated on a substrate 1 such as a 6 inch silicon wafer in diameter and prebaked by a hot plate at 90° C. for 90 seconds to give a resist material film 2 of 1.0 μm thick [FIG. 2 (*a*)]. The film 2 was selectively exposed to KrF excimer laser light 3 of 248.4 nm via a mask 4 at a dose of 25 mJ/cm^2 using a projection aligner (5:1 reduction, NA=0.42) [FIG. 2 (*b*)]. The exposed film was heated at 110° C. for 90 seconds, then development was carried out using a conventional alkali aqueous solution (2.38% tetramethylammonium hydroxide aqueous solution) for 60 seconds to remove exposed regions of the film 2 by dissolution to give a positive pattern 2*a* without loss of film thickness in the unexposed regions [FIG. 2(*c*)]. The positive pattern had an aspect ratio of ca. 87 degree and 0.3 μm lines and spaces were resolved.

APPLICATION EXAMPLES 2 to 7

Resist materials were prepared in the same manner as described in Application Example 1 except for using the diazodisulfone compounds obtained in Examples 2 to 7 as the photoacid generator. Patterns were formed on semiconductor substrates in the same manner as described in Application Example 1. The results are shown in Table 4.

TABLE 4

Application Example No.	Photoacid generator	Exposure energy amount (mJ/cm^2)	Resolution (μm L/S)
2	Example 3	25	0.3
3	Example 4	25	0.3
4	Example 5	30	0.3
5	Example 2	30	0.3
6	Example 6	30	0.3
7	Example 7	25	0.3

As is clear from Table 4, good positive tone patterns are formed by using the resist materials containing the compound of the formula (I) as the photoacid generator.

REFERENCE EXAMPLES 3 to 6

Resist materials were prepared in the same manner as described in Application Example 1 except for using the bis(straight-chain alkylsulfonyl)diazomethanes obtained in Comparative Examples 1 to 4. Using the resist materials, patterns were tried to form on semiconductor substrates in the same manner as described in Application Example 1, but no positive tone patterns were formed, since non-exposed portions were dissolved at the time of development.

These results show that the compounds of the formula (I) of the present invention obtained by introducing a bulky alkyl group into at least one of R^1 and R^2 moisties of the formula (I) play an important role to exhibit dissolution inhibiting effect for the alkali developing solution.

As mentioned above, when the photosensitive resist materials containing the diazodisulfone compounds of the formula (I) of the present invention are used for a light source of 300 nm or less such as deep UV light, KrF excimer laser light (248.4 nm), etc., fine patterns with good shapes of submicron order can easily be obtained.

The compound of the formula (I) of the present invention exhibits remarkable effects as the photoacid generator when exposed to not only deep UV light, KrF excimer laser light, but also ArF excimer laser light, electron beams, and X-rays.

What is claimed is:

1. A diazodisulfone compound of the formula:

(I)

wherein R^1 is a branched or cyclic alkyl group having 3 to 8 carbon atoms; and R^2 is a straight-chain, branched or cyclic alkyl group having 1 to 8 carbon atoms.

2. A diazodisulfone compound according to claim 1, wherein R^1 is a cyclopentyl group, a cyclohexyl group, an isopropyl group, a sec-butyl group, a tert-butyl group or an isoamyl group; and R^2 is a methyl group, an ethyl group, a cyclopentyl group, a cyclohexyl group, an isopropyl group, a sec-butyl group, a tert-butyl group or an isoamyl group.

3. A diazodisulfone compound according to claim 1, which is

bis(cyclohexylsulfonyl)diazomethane,
cyclohexylsulfonylethylsulfonyldiazomethane,
bis(isopropylsulfonyl)diazomethane,
bis(tert-butylsulfonyl)diazomethane,
bis(sec-butylsulfonyl)diazomethane,
tert-butylsulfonylmethylsulfonyldiazomethane,
tert-butylsulfonylcyclohexylsulfonyldiazomethane,
bis(cyclopentylsulfonyl)diazomethane,
cyclopentylsulfonyl-tert-butylsulfonyldiazomethane, or
bis(isoamylsulfonyl)diazomethane.

4. A diazodisulfone compound of the formula:

wherein R^1 is a branched or cyclic alkyl group having 3 to 8 carbon atoms; and R^2 is a branched or cyclic alkyl group having 3 to 8 carbon atoms.

5. A compound according to claim 4, wherein R^1 is a branched alkyl group having 3 to 8 carbon atoms; and R^2 is a branched alkyl group having 3 to 8 carbon atoms.

6. A compound according to claim 4, wherein R^1 is a cyclic alkyl group having 3 to 8 carbon atoms; and R^2 is a cyclic alkyl group having 3 to 8 carbon atoms.

7. A compound according to claim 4, wherein R^1 is a branched alkyl group having 3 to 8 carbon atoms; and R^2 is a cyclic alkyl group having 3 to 8 carbon atoms.

* * * * *

A diazodisulfone compound of the formula

Please add new claims 8 and 9 as follows:

8. A diazodisulfone compound of the formula;

$$\begin{array}{c} R^1SO_2CSO_2R^2 \\ \| \\ N_2 \end{array}$$

wherein R^1 is a cyclic alkyl group in which the alkyl group is hexyl; and R^2 is a cyclic alkyl group in which the alkyl group is hexyl.

9. A diazodisulfone compound of the formula;

$$\begin{array}{c} R^1SO_2CSO_2R^2 \\ \| \\ N_2 \end{array}$$

where R^1 is a branched alkyl group in which the alkyl group is butyl; and R^2 is a branched alkyl group in which the alkyl group is butyl.